Development of carbon membrane for CO_2/N_2 and CO_2/CH_4 separation

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Carbon membranes were prepared using stainless steel supports and evaluated for the separation of two mixtures, i.e. CO_2/N_2 and CO_2/CH_4. The effect of several operating variables, including temperature, pressure and precursor concentration was examined. In this study, carbon membranes were synthesized using a sucrose precursor. Sucrose was subjected to pyrolysis in the temperature range 300–700°C, leading to the complete formation of carbon structure. The gas separation characteristics of the produced membranes were estimated by evaluating CO_2, CH_4 and N_2 permeation. The highest selectivity obtained for CO_2/CH_4 and CO_2/N_2 was 1.64 and 1.41 respectively. The emphasis towards CO_2/CH_4 and CO_2/N_2 separation is due to their importance and direct relevance to the gas industry processes.

Keywords: Carbon membrane, greenhouse gases, pyrolysis temperature, separation mechanism, sucrose precursor.

INDUSTRIAL activities have led to an excessive increase of greenhouse gas (GHG) emission levels in the atmosphere[1]. Despite the fact that more energy resources from other non-fossil sources are being used in the industrial sector, fossil fuels are still considered as the main source[2]. CO_2 is a major GHG, and plays a significant role in climate change. The existing power plants worldwide are the main source and emit around 2 billion tonnes of CO_2 per year[2–5]. Therefore, the recovery of CO_2 from large emission sources is a difficult task confronting many developing countries. The separation of CO_2 from CH_4 and N_2 is important to be implemented in many industry-related processes, including natural gas sweetening, oil recovery enhancement, biogas upgrading and gas purification from landfill.

The identification of a separation/capture technology which would fulfil the needs of separation processes, with minimum energy consumption, is key and has attracted the attention of many researchers. Currently, the processes used for CO_2 separation are absorption, adsorption and cryogenic separation[5–8]. The conventional amine-based absorption technology is the most popular for CO_2 capture, as it is capable of achieving 90% of CO_2 capture from flue gas[9]. This is due to the fast kinetics along with the strong chemical reaction obtained[3,9]. Yet, absorption technology requires a significant amount of energy (4–6 MJ/kgCO_2) due to the significant energy ingested in the regeneration step[9–11]. On the other hand, membranes are a relatively novel separation technology and are considered to be a promising alternative to fulfil this task due to their simplicity, energy efficiency and as also being eco-friendly[12–14]. Nowadays, membranes are being studied for many separation applications, including CO_2 emissions capture from fossil fuel-based flue-gas streams[15–20]. They can consist of different material types, including organic (polymeric) and inorganic (carbon, zeolite, ceramic or metallic) with different structures, i.e. porous or non-porous[19–21]. Carbon membranes have been used in gas separation since 1970s, but the development of these types of membranes is yet to be studied[22–25]. Carbon membranes are produced by a pyrolysis procedure (heat-treatment process) using different types of precursors[26]. Yet, many precursors have not been explored and utilized[27]. In the present study, a simple sucrose precursor was used to produce carbon membranes through the pyrolysis process. Sucrose was chosen due to its natural resource and the fact that it can be produced without the extensive use of energy[28]. These membranes were subjected to CO_2 separation to determine their performance and effectiveness.

Experimental work

A thin carbon layer was prepared and supported using a porous stainless steel disc to provide mechanical strength. Before performing pyrolysis, the precursor solution was applied over the stainless steel support and left overnight to dry at room temperature. The sucrose solution was acquired by dissolving different amounts of sucrose in water to produce different concentrations by weight, i.e. 1 : 1, 2 : 1 and 3 : 1 ratios (sucrose : water). Pyrolysis was performed at 300°C and a heating rate of 2.5°C/min with soak time of 60 min using nitrogen as an inert gas. Table 1 lists the mass of carbon obtained.

Table 1 shows that higher concentrations have an accumulated amount of carbon mass due to their higher viscous properties. For further comprehension, the membranes were evaluated for CO_2/N_2 and CO_2/CH_4 permeation using a membrane gas unit (Convergance Inspector Neptunus). The experiments were performed at 25°C using feed

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pressure ranging from 5 to 15 bar and a feed flow rate of 100 l h^{-1}. The flux and selectivity of the carbon membrane were estimated using eqs (1) and (2) respectively. Usually, the permeability units used in membrane studies are the gas permeation unit (GPU) and Barrer.

$$P(\text{GPU}) = \frac{Q_i}{\Delta p \cdot A}, \tag{1}$$

$$\alpha_{A/B} = \frac{P_A}{P_B}, \tag{2}$$

where P_i is the flux, Q_i the volumetric flow rate of the gas, Δp the transmembrane pressure drop, A the surface area of the membrane and $\alpha_{A/B}$ is the separation factor/selectivity.

Results and discussion

The images obtained from a scanning electron microscopy (SEM), (JEOL, JSM-IT300) show carbon formation over the stainless steel support with thickness of around 36 μm (Figure 1). An electron-dispersive X-ray (EDX) spectrometer fitted with an INCA × act detector was utilized for additional characterization (Figure 2), indicating that the main components in the membrane are carbon, silica and alumina. Table 2 shows the performance of the membranes with different feed pressures and sucrose concentrations. It can be observed from the results that feed pressure is proportional to the fluxes and inversely proportional to selectivity, which illustrates the trade-off relation between these variables. With regard to precursor concentration, the solution concentration has significant influence on the overall performance in terms of flux and separation factor. Sucrose concentration is proportional to selectivity and inversely proportional to the flux. This is observed up to a certain limit (3 : 1), where the viscosity of the solution is very high and does not assist in the formation of a coherent carbon film. As a result, the membrane with the highest concentrated solution does not follow the pattern of the other three concentrations.

Thus it was concluded that the 3 : 1 concentration resulted in the highest selectivity of CO_2/CH_4, and hence it was taken for further analysis. Different pyrolysis temperatures were considered and evaluated to optimize the entire preparation procedure. Also, the membrane with 3 : 1 concentration was subjected to different pyrolysis temperatures, i.e. 300°–700°C (Table 3). As can be noted from the results, there is a decrease in the CO_2 and CH_4 fluxes with increase in the pyrolysis temperature. This may be due to the fact that higher pyrolysis temperature results in the narrowing of the pore structure, leading to an increase in membrane selectivity[29,30].

Table 3 clearly indicates that the membrane prepared at 600°C shows the best performance. This could be related to the coherent formation of carbon at this pyrolysis temperature. Therefore, the membrane prepared at 600°C was taken for further analysis performed using different feed pressures (5–15 bar) and different gases, i.e. CO_2, CH_4 and N_2 (Figures 3 and 4). Both CO_2/CH_4 and CO_2/N_2 followed the same performance pattern. However, the membrane was less selective to CO_2/N_2 due to similar molecule size of CO_2 and N_2 that will lead to more penetration of N_2 rather than CH_4, resulting in less selective performance. In other words, the permeability trend was inversely proportional to the kinetic diameter of these gases ($CO_2 < N_2 < CH_4$). This indicates the more rapid passing of gases with small-sized molecules through the membrane than the large ones, revealing that the permeation

Table 1. Weight of carbon membrane during preparation (1 : 1, 2 : 1 and 3 : 1 sucrose : water ratio)

	Carbon layer (weight in g)		
Membrane	1 : 1	2 : 1	3 : 1
Stainless steel disc	31.92	31.94	31.93
Stainless steel disc + sucrose	36.01	36.56	37.89
Membrane after pyrolysis	31.96	32.03	32.03
Mass of carbon	0.04	0.09	0.1

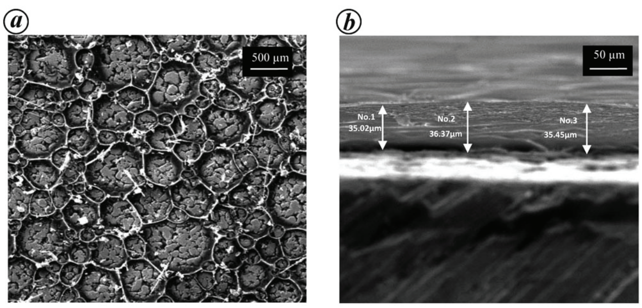

Figure 1. SEM images of (***a***) surface view and (***b***) edge view of carbon membrane with 3 : 1 concentration at magnification of 20 and 50 μm respectively.

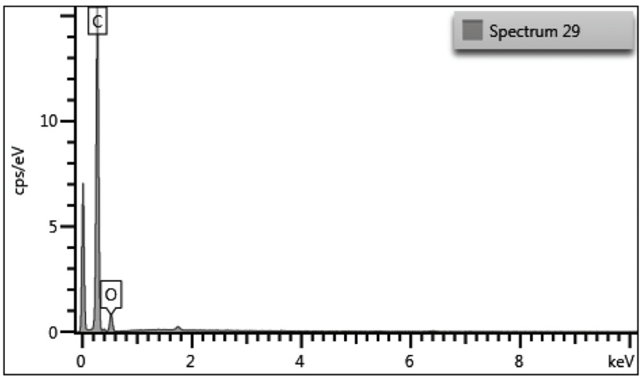

Figure 2. EDX membrane with 3 : 1 concentration.

Table 2. Selectivity and permeability of the prepared membranes at pyrolysis temperature of 300°C

Concentration sucrose : water	Feed pressure (bar)	Permeance (GPU) CO_2	Permeance (GPU) CH_4	Selectivity CO_2/CH_4
1 : 1	5	290.71	236.35	1.23
	7	442.69	365.87	1.21
	10	460.37	390.15	1.18
	15	448.13	400.12	1.12
2 : 1	5	283.07	199.35	1.42
	7	285.24	205.21	1.39
	10	290.56	213.65	1.36
	15	297.38	227.01	1.31
3 : 1	5	224.05	150.37	1.49
	7	233.56	159.97	1.46
	10	240.96	167.33	1.44
	15	258.82	180.99	1.43

Table 3. Permeability and selectivity of the membrane with concentration 3 : 1 at different pyrolysis temperatures and feed pressure of 5 bar

Pyrolysis temperature (°C)	Permeance (GPU) CO_2	Permeance (GPU) CH_4	Selectivity CO_2/CH_4
300	224.05	150.37	1.49
400	215.29	140.71	1.53
500	218.11	135.47	1.61
600	218.27	133.09	1.64
700	216.04	132.54	1.63

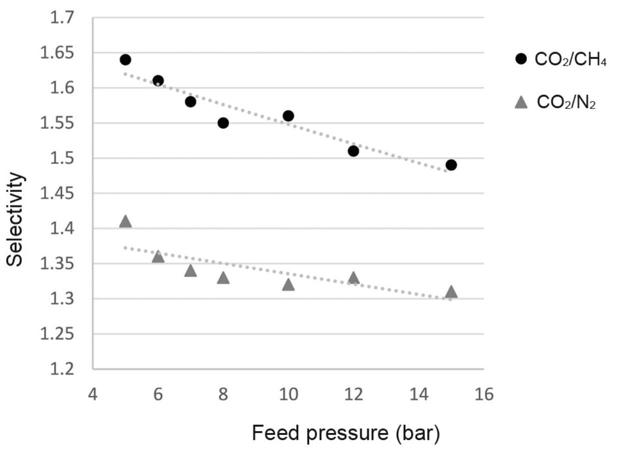

Figure 3. Effect of different feed pressures on membrane selectivity at 25°C.

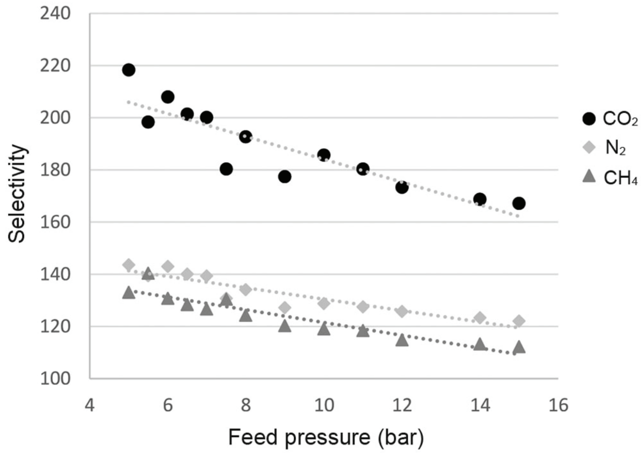

Figure 4. Effect of different feed pressures on membrane permeability at 25°C.

mechanism is related to the mechanism of molecular sieving rather than Kundsen diffusion. The results obtained from the membrane prepared in this study were compared with those reported in the literature (Tables 4 and 5). This reveals that more selective but less permeable polymeric membranes have been presented in the literature[31–39]. However, the main objective of this study was to avoid the costly and hazardous solvents used in the preparation of these conventional precursors using sucrose as the precursor compound.

The durability of the prepared membrane was tested and assessed. The membrane prepared at 600°C was subjected to pure CO_2 feed at 25°C and 5 bar. The durability/repeatability test was conducted for 7 h at different intervals. In general, the preparation method of fabricating carbon membranes for CO_2 separation yielded a stable performance during this period. This was evaluated by the variances (S^2) deviation in the data (eq. (3)). The membranes were permeating CO_2 within variances of 1.44. Other concentrations are expected to follow similar behaviours as they have been prepared using the same procedure.

$$S^2 = \frac{\sum_{i-1}^{n}(X_i - X_{\text{avg}})^2}{n-1}. \quad (3)$$

Conclusion

The preparation of selective carbon membrane was achieved successfully using a sucrose precursor for CO_2/

Table 4. Literature survey on selectivity and permeability of different membranes for CO_2 separation from CH_4

Membrane	Feed temperature (°C)	Selectivity	Permeance CO_2 (GPU)	Reference
Carbon	25	1.64	218.26	Present study
PDMS	25	32	110	31
Pebax	35	18	13.5	32
Polyvinylamine	25	23	81	33
Poly(4-vinylpyridine)/silico	35	29	92	34
Polyallylamine	50	15	112.5	35

Table 5. Literature survey on selectivity and permeability of different membranes for CO_2 separation from N_2

Membrane	Feed temperature (°C)	Selectivity	Permeance CO_2 (GPU)	Reference
Carbon	25	1.41	218.26	Present study
Oxydiphthalic anhydride	35	33.02	88.21	36
PSF	25	4.1	28	37
POEM	26	2.1	1.6	38
PVA	25	270	29	39
PDMS	25	35	110	31

CH_4 and CO_2/N_2 separation applications. The pyrolysis temperature is an important factor in determining the performance of the membrane that is produced in terms of selectivity and permeability. The results obtained from this study indicate that selectivity of the carbon membrane is proportional to pyrolysis temperature. This can be attributed to the fact that higher pyrolysis temperatures lead to the formation of a dense layer with narrow interplanar spacing, resulting in small pore structure. This eventually minimizes any pinholes and defects on the surface. A comparison between the permeability of different gases, i.e. CO_2, N_2 and CH_4, led to the conclusion molecular sieving is the dominant separation mechanism. In the literature, more selective carbon membranes using polymeric precursors have been reported[30]. However, the present overcomes the long process involved and toxic solvents used in the conventional precursors and preparation methods.

1. Torres, F., Gutierrez, J., Ruiz, L., Bertuzzi, M. and Erdmann, E., Comparative analysis of absorption, membrane, and hybrid technologies for CO_2 recovery. *J. Nat. Gas Sci. Eng.*, 2021, **94**, 104082.
2. Zeppini, P. and van den Bergh, J., Global competition dynamics of fossil fuels and renewable energy under climate policies and peak oil: a behavioural model. *Energy Policy*, 2020, **136**, 110907.
3. Benhelal, E., Shamsaei, E. and Rashid, M., Challenges against CO_2 abatement strategies in cement industry: a review. *J. Environ. Sci.*, 2021, **104**, 84–101.
4. Song, C., Liu, Q., Deng, S., Li, H. and Kitamura, Y., Cryogenic-based CO_2 capture technologies: state-of-the-art developments and current challenges. *Renew. Sustain. Energy Rev.*, 2019, **101**, 265–278.
5. Borgohain, R., Pattnaik, U., Prasad, B. and Mandal, B., A review on chitosan-based membranes for sustainable CO_2 separation applications: mechanism, issues, and the way forward. *Carbohydr. Polym.*, 2021, **267**, 118178.
6. Solangi, N., Anjum, A., Tanjung, F., Mazari, S. and Mubarak, N., A review of recent trends and emerging perspectives of ionic liquid membranes for CO_2 separation. *J. Environ. Chem. Eng.*, 2021, **9**(5), 105860.
7. Godin, J., Liu, W., Ren, S. and Xu, C., Advances in recovery and utilization of carbon dioxide: a brief review. *J. Environ. Chem. Eng.*, 2021, **9**(4), 105644.
8. Tomić, L., Danilović, D., Karović-Maričić, V., Leković, B. and Crnogorac, M., Application of membrane technology for separation of CO_2 from natural gas. *Podzemni Radovi*, 2020, **36**, 61–68.
9. Kiani, A., Jiang, K. and Feron, P., Techno-economic assessment for CO_2 capture from air using a conventional liquid-based absorption process. *Front. Energy Res.*, 2020, **8**, 8–18.
10. Ooi, Z., Tan, P., Tan, L. and Yeap, S., Amine-based solvent for CO_2 absorption and its impact on carbon steel corrosion: a perspective review. *Chin. J. Chem. Eng.*, 2020, **28**(5), 1357–1367.
11. Chakravartula Srivatsa, S. and Bhattacharya, S., Amine-based CO_2 capture sorbents: a potential CO_2 hydrogenation catalyst. *J. CO_2 Util.*, 2018, **26**, 397–407.
12. Baker, R., *Membrane Technology and Applications*, Wiley, Hoboken, NJ, USA, 2013.
13. Strathmann, H., Giorno, L. and Drioli, E., *Introduction to Membrane Science and Technology*, Wiley-VCH Verlag and Company, Germany, 2011.
14. Iulianelli, A. and Drioli, E., Membrane engineering: latest advancements in gas separation and pre-treatment processes, petrochemical industry and refinery, and future perspectives in emerging applications. *Fuel Proc. Technol.*, 2020, **206**, 106464.
15. Ramírez-Santos, Á., Bozorg, M., Addis, B., Piccialli, V., Castel, C. and Favre, E., Optimization of multistage membrane gas separation processes. Example of application to CO_2 capture from blast furnace gas. *J. Membr. Sci.*, 2018, **566**, 346–366.
16. Kamble, A., Patel, C. and Murthy, Z., A review on the recent advances in mixed matrix membranes for gas separation processes. *Renew. Sustain. Energy Rev.*, 2021, **145**, 111062.
17. Brunetti, A., Scura, F., Barbieri, G. and Drioli, E., Membrane technologies for CO_2 separation. *J. Membr. Sci.*, 2010, **359**(1–2), 115–125.
18. Scofield, J., Gurr, P., Kim, J., Fu, Q., Kentish, S. and Qiao, G., Development of novel fluorinated additives for high performance CO_2 separation thin-film composite membranes. *J. Membr. Sci.*, 2016, **499**, 191–200.
19. Singh, S., Varghese, A. and Karanikolos, G., Mixed matrix CO_2 separation membranes based on polysulfone with Cu-BTC metal–organic framework and poly(ethylene glycol)-grafted carbon nanotubes. *SSRN Electron. J.*, 2021, **2**, 193–206.

20. Han, Y. and Ho, W., Polymeric membranes for CO_2 separation and capture. *J. Membr. Sci*., 2021, **628**, 119244.
21. Yang, Z. *et al*., A critical review on thin-film nanocomposite membranes with interlayered structure: mechanisms, recent developments, and environmental applications. *Environ. Sci. Technol*., 2020, **54**(24), 15563–15583.
22. Alomair, A., Al-Jubouri, S. and Holmes, S., A novel approach to fabricate zeolite membranes for pervaporation processes. *J. Mater. Chem. A*, 2015, **3**(18), 9799–9806.
23. Chen, X., Kaliaguine, S. and Rodrigue, D., Correlation between performances of hollow fibers and flat membranes for gas separation. *Separ. Purif. Rev*., 2017, **47**(1), 66–87.
24. Jones, C. and Koros, W., Carbon molecular sieve gas separation membranes-I. Preparation and characterization based on polyimide precursors. *Carbon*, 1994, **32**(8), 1419–1425.
25. Ning, X. and Koros, W., Carbon molecular sieve membranes derived from Matrimid® polyimide for nitrogen/methane separation. *Carbon*, 2014, **66**, 511–522.
26. Wei, W., Qin, G., Hu, H., You, L. and Chen, G., Preparation of supported carbon molecular sieve membrane from novolac phenol–formaldehyde resin. *J. Membr. Sci*., 2007, **303**(1–2), 80–85.
27. Ismail, A. and David, L., A review on the latest development of carbon membranes for gas separation. *J. Membr. Sci*., 2001, **193**(1), 1–18.
28. Sazali, N., Salleh, W., Nur Izwanne, M., Harun, Z. and Kadirgama, K., Precursor selection for carbon membrane fabrication: a review. *J. Appl. Membr. Sci. Technol*., 2018, **22**(2).
29. Alomair, A., Alqaheem, Y. and Holmes, S., The use of a sucrose precursor to prepare a carbon membrane for the separation of hydrogen from methane. *RSC Adv*., 2019, **9**(19), 10437–10444.
30. Lei, L., Bai, L., Lindbråthen, A., Pan, F., Zhang, X. and He, X., Carbon membranes for CO_2 removal: status and perspectives from materials to processes. *Chem. Eng. J*., 2020, **401**, 126084.
31. Zulhairun, A., Fachrurrazi, Z., Nur Izwanne, M. and Ismail, A., Asymmetric hollow fiber membrane coated with polydimethylsiloxane–metal organic framework hybrid layer for gas separation. *Separ. Purif. Technol*., 2015, **146**, 85–93.
32. Esposito, E. *et al*., Pebax®/PAN hollow fiber membranes for CO_2/CH_4 separation. *Chem. Eng. Process*., 2015, **94**, 53–61.
33. He, X., Kim, T. and Hägg, M., Hybrid fixed-site-carrier membranes for CO_2 removal from high pressure natural gas: membrane optimization and process condition investigation. *J. Membr. Sci*., 2014, **470**, 266–274.
34. Qin, J. and Chung, T., Development of high-performance polysulfone/poly(4-vinylpyridine) composite hollow fibers for CO_2/CH_4 separation. *Desalination*, 2006, **192**(1–3), 112–116.
35. Cai, Y., Wang, Z., Yi, C., Bai, Y., Wang, J. and Wang, S., Gas transport property of polyallylamine–poly(vinyl alcohol)/polysulfone composite membranes. *J. Membr. Sci*., 2008, **310**(1–2), 184–196.
36. Chuah, C., Lee, J., Song, J. and Bae, T., CO_2/N_2 separation properties of polyimide-based mixed-matrix membranes comprising UiO-66 with various functionalities. *Membranes*, 2020, **10**(7), 154.
37. Oh, J., Kang, Y. and Kang, S., Poly(vinylpyrrolidone)/KF electrolyte membranes for facilitated CO_2 transport. *Chem. Commun*., 2013, **49**(86), 10181.
38. Park, C., Lee, J., Jung, J., Jung, B. and Kim, J., A highly selective PEGBEM-g-POEM comb copolymer membrane for CO_2/N_2 separation. *J. Membr. Sci*., 2015, **492**, 452–460.
39. Mondal, A. and Mandal, B., CO_2 separation using thermally stable crosslinked poly(vinyl alcohol) membrane blended with polyvinylpyrrolidone/polyethyleneimine/tetraethylenepentamine. *J. Membr. Sci*., 2014, **460**, 126–138.

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